

Structural characterisation of lanthanum aluminate synthesized by the Pechini method

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Single phase LaAlO₃ fine particles were prepared by Pechini method at low-temperature. The method involved the mixing of the nitrates of La and Al, with a chelating agent, a mix 1:1 of citric acid and ethylene glycol. The powders were studied by several physical characterization techniques such as X-ray diffraction (XRD), thermal analysis (TG-DTG) and high-resolution electron microscopy (HRTEM). The TEM photographs reveal nano-particles in the size range 20 – 90 nm with a mean diameter of about 50 nm.

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1. Introduction

Lanthanum aluminate (LaAlO₃), which belongs to the perovskite type oxide materials, has been widely used as a substrate of high-temperature superconductor and ferroelectric thin films due to their low dielectric loss and minor lattice mismatch between the substrate and film [1-6]. For practical applications, high- T_c superconducting thin films on silicon or sapphire substrates with a LaAlO₃ buffer layer have better properties than those applied directly on the single crystal substrates [7]. Other uses of LaAlO₃ which have attracted much attention are in the gas sensors [8] and as catalyst for oxidative coupling of methane and hydrogenation and hydrogenolysis of hydrocarbons [9].

The common method of preparation of LaAlO₃ is the solid state reaction method [10]. The direct formation of LaAlO₃ from aluminum oxide (Al₂O₃) and lanthanum oxide (La₂O₃) occurs typically in the range of 1500 – 1700°C, with melting occurring at about 1830°C. This conventional ceramic method involving the direct combination of the corresponding oxides by thermal treatment at high temperature and ball-milling is not adequate for many advanced applications and suffers from many inherent shortcomings. Problems have arisen with poor sintering behavior and non-homogeneity, which have a detrimental effect on the electrical and mechanical properties. Sung et al. [10] reported the full development of LaAlO₃ phase only on heating the sample to 1600°C and they needed to reheat the same sample to 1750°C for 3 h to form a polycrystalline disk to be used as a target for radio-frequency magnetron sputtering of LaAlO₃ thin films as buffer layers on silicon wafers.

Many attempts have been made to lower the synthesis temperature using different preparation routes such as the co-precipitation [11], aerosol combustion [12,13], in situ polymerization, sol-gel and polycarboxylic acid complexation. Li et al. [11] achieved nanosized powders by co-precipitation from nitrate salts at constant pH. Kumar et al. [14] produced LaAlO₃ by thermal

decomposition using hydrated nitrate precursors. Adak and Pramaniak [15] used polyvinyl alcohol as a matrix for handling uniform solid nitrate mixtures. Behera et al. [16] observed the effect of ultrasonication on the precipitation route. The main drawback for the powders obtained from the co-precipitation technique is the highly agglomerated nature a further ball-milling being necessary to obtain fine powders with small particle size. Although all the above-mentioned methods have been successful in obtaining lanthanum aluminate, better or new route are still required to obtain pure and homogeneous LaAlO₃ powders with small particle size at relatively low temperature for commercial production.

The sol-gel method and its modifications have been widely used for inorganic/ceramic, catalytic materials and also organic-inorganic hybrid structures [17-19]. The success of the sol-gel process in the synthesis of ceramic powders is due, in particular, to the possibility of working at low temperatures and attaining good homogeneity in the solution phase. A process related to the sol-gel route is the Pechini method or liquid mix process [20]. An important consequence of the molecular-scale mixing is a drastic reduction in the calcination temperature. Also the particle size is extremely small, typically 30 to 60 nanometres.

We report here on the synthesis and structural characterization of lanthanum aluminate nanopowders obtained by the Pechini method. The LaAlO₃ nanopowders have been investigated by thermal analysis (TG-DTG), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), and selected area electron diffraction (SAED).

2. Experimental

2.1. Materials

Single phase lanthanum aluminate LaAlO₃ with fine particles were prepared by polymerized complex method using citric acid and ethylene glycol route (Pechini method

[20]). The method involved the mixing of either nitrates of metals, La and Al, with a chelating agent, a mix 1:1 of citric acid and ethylene glycol. Also the ratio of La:Al was 1:1. The nitrate salts are favoured as precursors because they serve as water-soluble at low temperature and nitrogen source for the synthesis. The mix of citric acid and ethylene glycol acted as fuels decomposed the homogeneous precipitate of metal complexes at low temperature. The reactants were dissolved in deionised water. Initially the solution boiled and dehydrated followed by decomposition, releasing copious amounts of heat and gases. The mixture slowly turned into a highly viscous gel. On further heating the gel swelled into foam of fine flakes and got ignited with evolution of large quantity of gases yielding foamy powder of lanthanum aluminate. The foamy powders were then hand ground in an agate mortar and were heat-treated between 700 – 1000°C during 3 hours.

2.2. Methods

The powders were studied by several physical characterization techniques such as X-ray diffraction (XRD) and high-resolution electron microscopy (HRTEM). XRD data were obtained using an X-ray Shimadzu XRD 6000 diffractometer with $\text{CuK}\alpha$ radiation. Thermal analysis (TG-DTG) was performed using a MOM type C instrument in air with the temperature in the range of 20 – 900°C and the heating rate of 10°C/min. High-resolution electron microscopy, performed with a Philips CM 120 ST electron microscope operating at 100 kV and allowing a magnification of up to 1,200,000x and a resolution as low as 2Å, was used to evaluate the purity and the phase composition of LaAlO_3 . The selected area electron diffraction examination (SAED) allowed the identification of the lattice planes, giving information about the crystal structure.

3. Results and discussion

The thermal decomposition and crystallization behavior of the lanthanum aluminate precursor is represented by thermogravimetric (TG) and differential thermogravimetric (DTG) curves shown in Fig. 1.

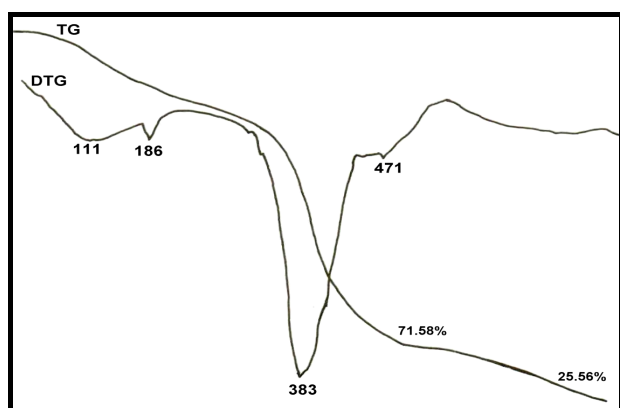


Fig. 1. TG-DTG curves of the LaAlO_3 precursor powder.

Fig. 1 reveals four main endothermic events at 111, 186, 383 and 471°C, respectively. At temperatures below 111°C, 7.23% weight decrease is assigned to the loss of moisture from the washed precursor powders. Apparently, the endothermic peak at 186°C with 10.38% weight loss is due to the dehydration of the precursor powders. The third endothermic peak at 383°C with 53.97% (total 71.58%) weight loss is attributed to the decomposition of $\text{LaAl}(\text{OH}(\text{CO}_3))_2$ into LaAlO_3 .

The XRD spectra of the LaAlO_3 powders heated in the range 700-900°C, for 3 hours, in dry air are plotted in Fig. 2. The XRD peaks were indexed in terms of perovskite structure according to the JCPDS card 31-0022. A peak of the LaAlO_3 phase with rather weak intensity appeared at 600°C and no intermediate phases at post-heated treated particles were observed. This means that LaAlO_3 was the only crystalline phase to form during the annealing process, indicating higher cation homogeneity of the precursor. Increasing the annealing temperature leads to an increase of the intensity (see Fig. 2).

The intensity of the XRD peaks grows with increasing the temperature suggesting better crystallinity for the powders obtained at 900°C. These results, clearly indicate that pure-phase LaAlO_3 could be synthesized directly by the Pechini method at low crystallization temperatures.

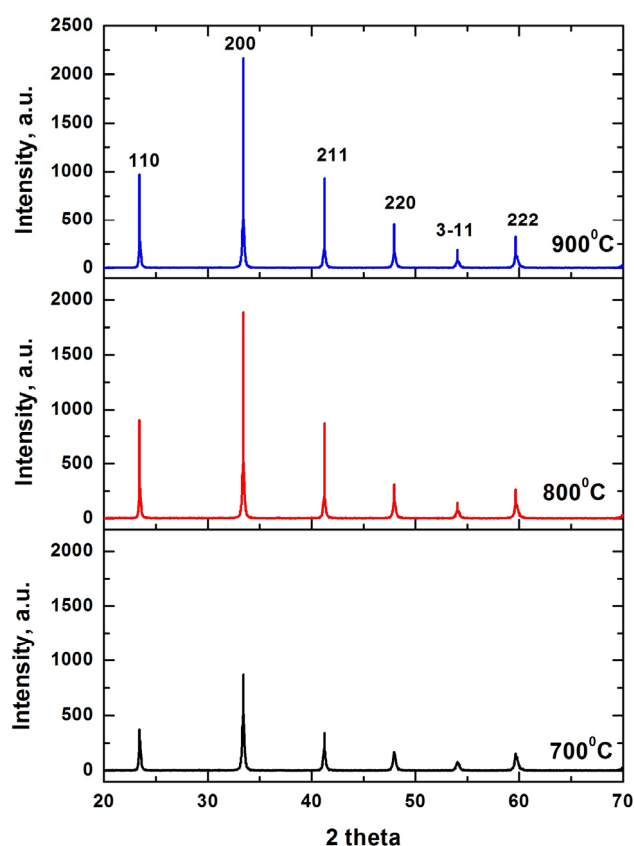


Fig. 2. X-ray diffraction patterns of LaAlO_3 powders grown by the sol-gel technique.

In Fig. 3 is presented the intensity of XRD spectra as a function of the thermal treatment temperature for synthesized LaAlO_3 heated in the range 600 – 1000°C. One can observe that increasing the annealing temperature up to 900°C leads to a powder with higher crystallinity.

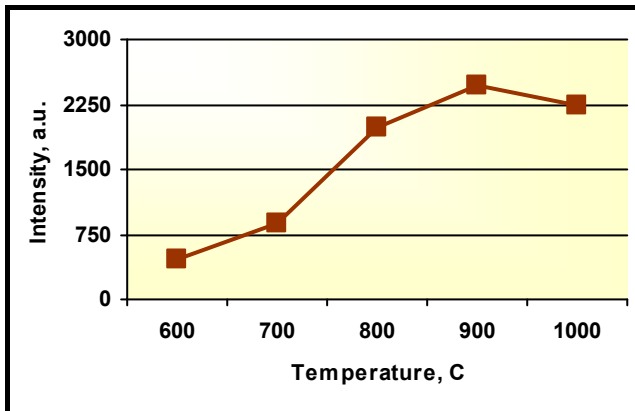


Fig. 3. The intensity of the main XRD peak (3.80 Å) as a function of the annealing temperature.

The results obtained by XRD were confirmed by selected area electron diffraction (SAED) image. The structure of the compound is trigonal in most cases at lower temperature, belonging to the $R\text{-}3c$ space group, with lattice constants $a = 0.536$ nm and $c = 1.311$ nm. In Fig. 4 is presented the electron diffraction pattern of 900°C LaAlO_3 compound. The left insert show a list of indexed plane corresponding to marked rings on figure.

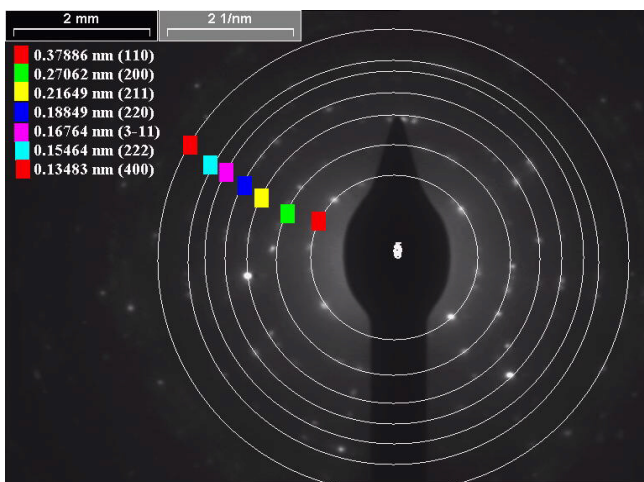


Fig. 4. SAED image of LaAlO_3 sample prepared at 900°C.

Fig. 5 presents a HRTEM image that reveals the presence of the crystalline plane (110) on a grain. The bottom-left corner insert represents a FFT space representation of the HRTEM image, which allowed us to estimate the interplanar distance.

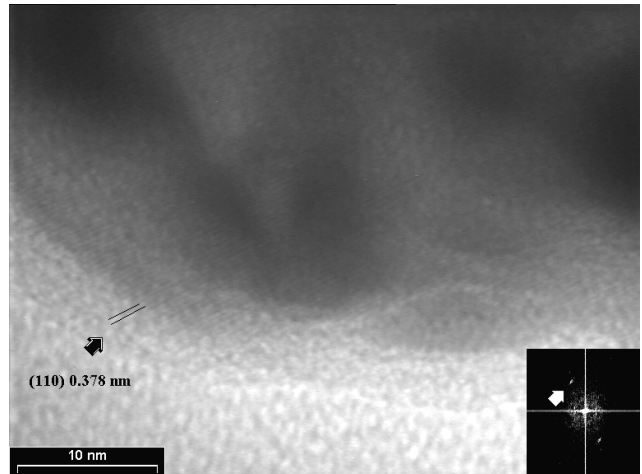


Fig. 5. HRTEM image showing the (110) plane. Inset with a FFT of the image.

The morphology and mean diameter were studied using a bright-field (BF) TEM micrograph. The TEM microstructure of the LaAlO_3 gel powders annealed at 900°C for 3h is shown in Fig.6. The BF-TEM micrograph of the LaAlO_3 powder indicates that the nanocrystallites have a roughly spherical morphology with an average diameter ranging from 20 to 90 nm.

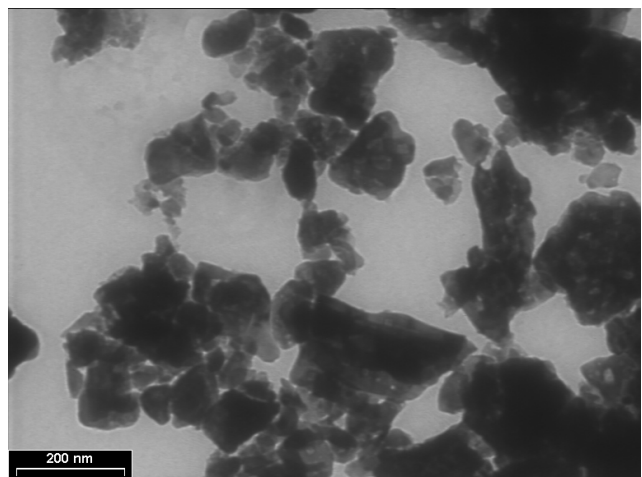


Fig. 6. BF - TEM image of LaAlO_3 sample prepared at 900°C.

The particle diameter is evaluated by the mean value of the distances between pairs of parallel tangents to the projected outline of the particle (Feret's diameter) and the mean diameter is calculated assuming a lognormal distribution of the experimental data. Fig. 7 present lognormal distribution curves for mean diameter.

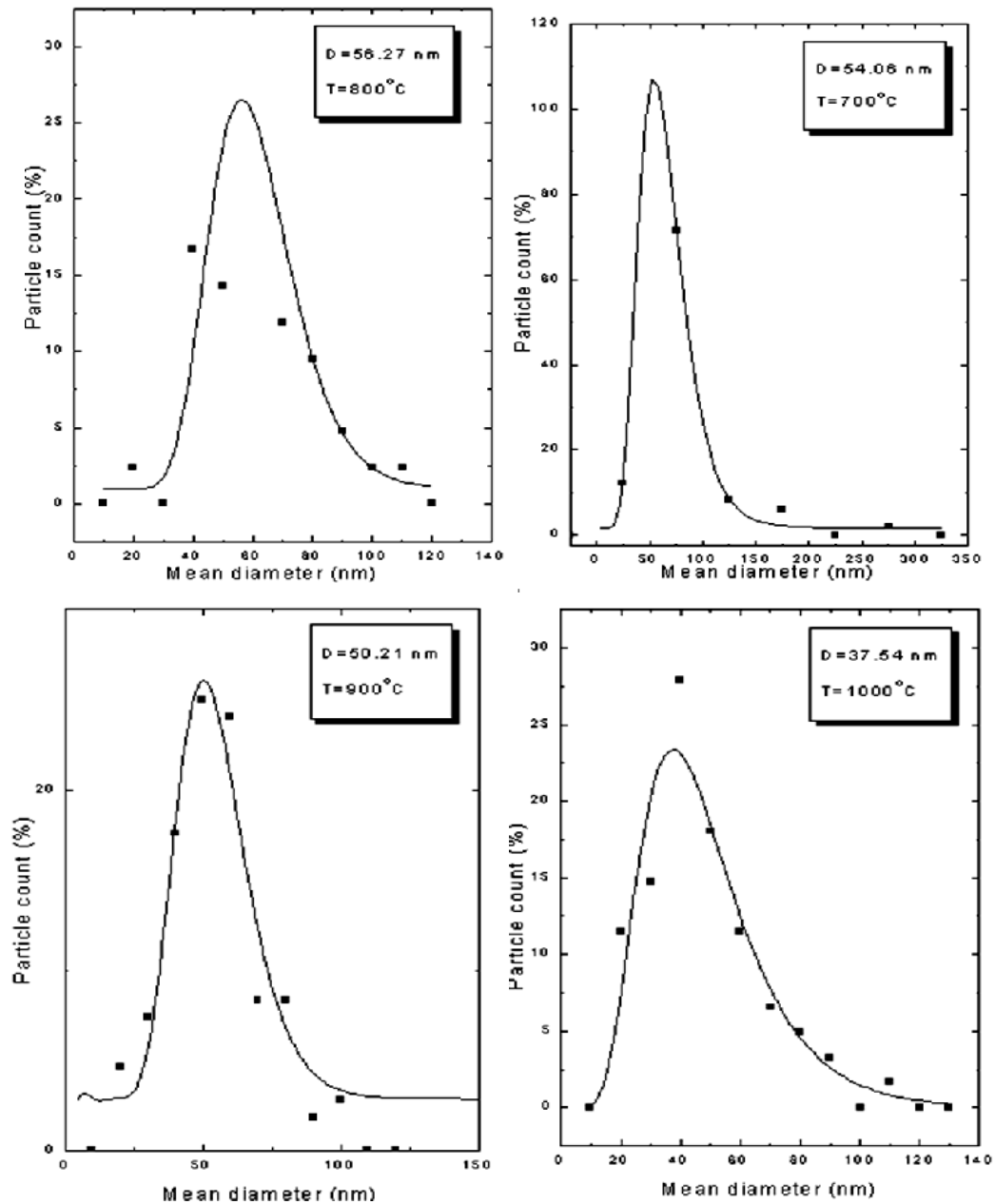


Fig. 7. The distribution of grain sizes for LaAlO_3 samples prepared at various temperatures (700, 800, 900 and 1000°C) and the log-normal fit of the data.

The grain size distribution was fitted to a log-normal function, $y = y_0 + A \cdot \exp\left[-\frac{\ln^2(x/x_c)}{2w^2}\right]$, where y_0

is a baseline, A a constant related to the number of particles analyzed, x_c is the size of the distribution maximum, whereas w is correlated with the dispersion of the particle diameters [21]. The results for different temperatures are summarized in Table 1.

Table 1. Fitting parameters of the distribution of particle diameters resulted from the analysis shown in Fig. 7.

T (°C)	x_c (nm)	w
700	54.06	0.36
800	56.27	0.24
900	50.21	0.25
1000	37.54	0.42

We note that the particle sizes tend to decrease as the annealing temperature increases over 900°C because of the growth and aggregation of the powders at higher temperature. Also the width of the grain size distribution increases at higher annealing temperatures.

4. Conclusions

We reported original contributions to the synthesis and structural characterization of LaAlO₃ nanocrystalline powders. The lanthanum aluminate was obtained by the Pechini method, starting from La(NO₃)₃ and Al(NO₃)₃ using a mix of citric acid and ethylene glycol (1:1) as chelating agent, followed by a thermal treatment at temperatures up to 1000°C. We showed that the Pechini method can dramatically lower the crystallization temperature of LaAlO₃ by about 600°C compared to the classical solid-state reaction method, such that the formation of LaAlO₃ synthesized by this method is complete at 900°C. The XRD analysis showed sharp peaks LaAlO₃, indicating that the powder obtained by the Pechini method consists of nanocrystalline grains. The TEM images demonstrated that the nanocrystalline LaAlO₃ particles have a roughly spherical morphology with an average diameter ranging from 20 to 90 nm. The mean diameters of the LaAlO₃ synthesized at 900°C were about 50 nm, higher annealing temperature leading to a decrease of the sizes of the nanocrystallites. We also showed that the structure of LaAlO₃ is trigonal (space group *R-3c*), with lattice parameters *a* = 0.536 nm, *c* = 1.311 nm.

Our results prove the superiority of this synthesis route, the organic phase (component of the reaction mixture) having a double role, in carrying the La³⁺ and Al³⁺ ions and in heat generation, which, likely, are the key factors that contribute to the early formation of LaAlO₃.

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